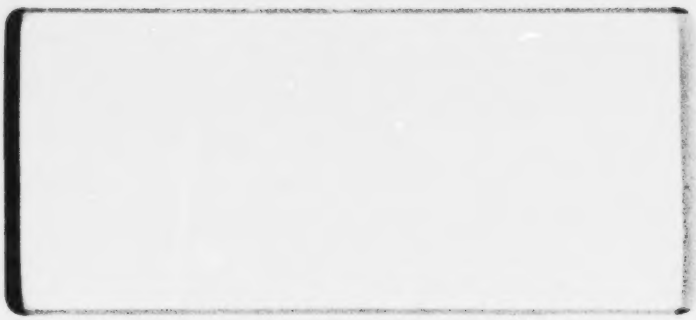

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TREATMENT OF SYNTHETIC CRUDES WITH METAL CHLORIDES AND METAL CARBONYLS

Final Report

by

K. R Dymock
M. J. Giampuzzi

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OBJECTIVE

To develop novel concepts for segregation of nitrogen and/or sulphur compounds from synthetic crudes.

The specific objectives of this proposal are to determine the separability of specific sulfur and nitrogen species from hydrotreated Syncrude gas oil by:

i) precipitation with a metal chloride
ii) extraction into a polar solvent containing a metal complex
iii) precipitation with a metal carbonyl or hydrido carbonyl compound
iv) hydrogenation of metal carbonyl and/or hydrido carbonyl-problematic component complexes.

BACKGROUND

The majority of Canada's fossil fuel resources are tar sands, heavy oil and coal. These materials, when converted to synthetic crudes, produce liquids which are rich in nitrogen and sulfur species as well as containing considerable amounts of high boiling heavy ends. This implies that the removal of nitrogen and sulfur compounds from heavier fractions is of primary importance since their effective elimination would reduce or eliminate the need to remove their cracked products from lower boiling transportation fuels, such as gasoline and middle distillate.

The presence of mercaptans, sulfides and thiophenes in fuels decrease response to octane improvers in fuels and result in corrosion of engine parts, brass and copper. Also, polycyclic aromatic bases, such as quinolines and acridines, have been found to poison fluid catalytic cracking catalysts [1].

Although a variety of commercially proven processes are available for removing sulfur compounds, the options for denitrogenation are more limited. Liquid extraction of the oil, using mineral acids, poses serious problems due to emulsions [2]. Denitrogenation by hydrotreating requires more severe conditions than hydrodesulphurization and results in non-selective saturation of non-nitrogeneous components.

Precipitation with metals has been used commercially in the petroleum industry to desulphurize both gasolines and middle distillates manufactured from sour crudes [3]. Copper sweetening employs cupric chloride to convert mercaptans to disulphides in gasoline boiling range materials, while the doctor treatment uses sodium plumbite to accomplish the same conversion [3].

Choi and Dines [4] reported that nitrogen compounds can be selectively removed from aromatic systems by reaction with solid Lewis acids. This project will explore this approach further by assessing the ability of Lewis acids and transition metal complexes to act as extractants for sulfur and nitrogen species.

Precipitation is generally not favoured in industrial processes because it is expensive, labour intensive and troublesome. Therefore, if a metal salt could be dissolved in a hydrocarbon immiscible solvent, problematic components may be selectively extracted due to the formation of stable or, better yet, semistable coordination complexes The use of metals in commercial processes as intermediates is not new, and metal complexes have been used successfully in several separations. Copper ammonium acetate is used to separate carbon monoxide from synthesis gas due to the formation of a semistable copper carbon monoxide forming a metal complex. What this suggests is the reverse process, i.e. extracting the problematic component from a hydrocarbon phase into an immiscible solvent containing metal.

Metal carbonyls and hydridocarbonyls particularly those of iron, react vigorously with both nitrogen and sulfur compounds [5,6]. The reactions involve not only simple complexation but ring opening and, in some instances, heteroatom elimination. The metal carbonyls and hydridocarbonyls are readily manufactured from the metal, and carbon monoxide. They have various degrees of reactivity but diironnonacarbonyl is of particular interest, since it has been shown to be very effective at both nitrogen and sulfur removal during primary coal liquefaction [7] and it is insoluble in all solvents since it is an inorganic polymer. This is exceptional since the liquefaction of these materials occurs at severe reaction conditions (5000 psig, 450°C).

Metal carbonyls and hydridocarbonyls are also used as homogeneous catalysts in a number of industrial processes [7]. These include hydroformylation (dicobalt octacarbonyl and cobalt hydrocarbonyl), acrylic acid synthesis (nickel tetracarbonyl), and carbonylation of methanol (rhodium carbonyl iodide) The utility of these catalysts is based on the complexes they form with hydrogen, carbon monoxide and a ligand which allow high energy conversions to occur readily and with specificity. Complexation of the problematic components in the synthetic test blend with various carbonyl compounds may make the complex readily amenable to hydrodesulphurization and hydrodenitrification.

The complexation of inorganic molecules with various problematic components suggest a novel approach to eliminating these species from Synthetic crude gas oils. With the use of a synthetic blend of known composition, precipitation, back extraction and hydrogenation of problematic component complexes can be scoped to assess their usefulness.

EXPERIMENTAL

Overview

A synthetic test blend was prepared from four nitrogen and four sulfur containing model compounds typical of the problematic components in synfuels. The synthetic test blend was used to calibrate the gas chromatographs as described below.

The synthetic test blend was contacted with solid metal chlorides, at 25°C for 1 h and at 200°C for 1 h, extracted with immiscible polar organic solvents which contained known quantities of metal chloride, contacted with metal carbonyls at 25°C for 30 min and at 100°C for 10 min., and hydrogenated at 1000 psig H_2 at 100°C for 2 h.

1. Preparation of Synthetic Test Blend

A 1000 ppm Nitrogen and Sulfur synthetic test blend was prepared according to the proportions given in Table 1. Characteristics of the hydrotreated middle distillate, Syncrude Light Distillate, which was used in the synthetic test blend, are detailed in Table 2.

Typically the synthetic test blend was prepared in 500 mL aliquots. The following procedure was used.

The solid problematic components were weighed into a 1 L flask using a Mettler Gram-A-Tic balance, followed by weighing in of the Syncrude light distillate using a Mettler P5N balance; the dodecyl mercaptan and dinonyl sulfide were measured volumetrically in a Hamilton 1.0 mL syringe and added by immersing the syringe needle into the mixture. The solution was mixed and heated to 100°C and shaken on a mechanical shaker until a clear solution was obtained (3-4 h). The synthetic test blend was sealed and stored in a refrigerator (9°C) up to 48 h.

2. Quantitation of Nitrogen Containing Problematic Components

Instrument Calibration

The synthetic test blend was diluted 1:1 in acetone containing 100 ppm N as quinoline. The diluted sample was injected onto the Varian 3700 several times, in 0.1 µL aliquots. Chromatographic output was collected by the Perkin Elmer 3200, and peak areas for quinoline, 2 methyl-indole, carbazole, 7,8 benzoquinoline and N-ethylcarbazole were collected. The response factors, using quinoline as the internal standard, were calculated and are given in Table 3. Linearity of response had been previously demonstrated using dimethyl-pyridine and 2-methylpyridine (8). The instrument conditions used for these analyses are given in Table 3.

Sample Analysis

Samples were analyzed by diluting them 1:1 in acetone containing 100 ppm N as quinoline as an internal standard and injecting 0.1 µL aliquots on the Varian 3700 using the parameters listed in Table 3.

3. Quantitation of Sulfur Containing Problematic Problems

Instrument Calibration

The synthetic test blend was diluted in the following ratios in Syncrude light distillate:

(Syncrude light distillate: synthetic test blend)

1:9, 1:4, 3:7, 2:3, 1:1, 7:3, 9:1

Each of these solutions was subsequently diluted 1:9 in acetone to allow larger volumes to be injected and minimize injection error. 1.0 µL volumes were injected and peak heights were measured manually. All calibrants were run in one working day to minimize error due to day-to-day variation The synthetic test blend was injected at the beginning and end of each day to ensure detector response did not change significantly. Calibration data is summarized in Table 4. Instrument conditions are also given in Table 4. Calibration data was plotted on log paper and the response functions given in Table 4 were generated.

Sample concentrations were determined by diluting them 1:9 in acetone and injecting 1.0 µL quantities onto the Perkin Elmer 3920 (set up as detailed in Table 4). Peak heights were determined manually, and the response equations (Table 4) were used to convert peak height into concentrations.

Dodecyl mercaptan was found to oxidize and disappear from the chromatogram in less than 8 hours. Its concentration was back calculated from total sulfur measured by x-ray fluorescence and the analysis of other sulphur species.

4. Treatment with Metal Chlorides, 1 h 25°C

A 10% stiochiometric excess (in 1:1 mole %) of metal chloride (available from Fisher Scientific Inc.) was weighed into a 200 mL Erlenmeyer flask. 50 mL of synthetic test blend was added and the solution was stirred using a magnetic stirrer at medium speed for 1 hour. Changes in visual appearance were noted and are given in Table A. The solutions were filtered through a Whatman #4A filter paper and the filtrate was analyzed by GC. GC results are given in Table 8.

Quantities of metal chloride used are listed in Table A as well as the experimental observations.

5. Treatment with Metal Chlorides, 2 hours, 200°C

A 10% stoichiometric excess of metal chloride was weighed into a 200 mL round bottom flask with thermometer well. 50 mL of synthetic test blend was added and the flask was fitted with a heating mantle, condenser and thermometer. The solution was heated to 200°C and maintained at this temperature for 2 hours. The solution was allowed to cool to room temperature overnight, after which it was filtered through a Whatman 4A filter paper, and analyzed by GC. Observations are given in Table A. The quantities of metal chloride used are identical to those given above.

6. Extraction with Polar Organic Solvents

Aliquots of metal chloride and 20 mL of various solvents were combined in 100 mL bottles in a square matrix design to yield 35 combinations. The bottles were capped and the solutions were kept at room temperature for 48 hours.

20 mL of synthetic test blend was added to each bottle and the samples were shaken on a mechanical shaker at high speed for 1 hour. The samples were left undisturbed for 3 hours and then a 1 mL sample of the hydrocarbon phase was submitted for GC analysis. The following aliquots of metal chloride were used: 0.15 g $CuCl_2.2H_2O$, 0.226 g $FeCl_3.6H_2O$, 0.166 g $SnCl_2$, 0 120 g $ZnCl_2$, 0 233 g C_2H_5HgCl, 0.276 g C_6H_5HgCl. The following solvents were used: DMSO DMF CH_3CN NMP, furfural. All metal chlorides were soluble, except C_6H_5HgCl in CH_3CN. The undissolved C_2H_5HgCl was filtered off, and the C_6H_5HgCl filtrate was used for subsequent extractions. NMP containing samples did not separate into two phases. Observations are given in Table B.

7. Treatment With Metal Carbonyls

A 10% stoichiometric excess of metal carbonyl was added to a 100 mL Erlenmeyer flask. 50 mL of synthetic test blend, and a stirring bar were added The solution was stirred for 30 min at 25°C. A 1 mL sample was taken and submitted for GC analysis. The remaining 49 mL were transferred to a 200 mL round bottom flask with a thermometer well.

A heating mantle, thermometer and a condensor were attached. The solution was heated to 100°C and maintained there for 10 min. The solution was removed from the heat source and allowed to return to room temperature before being filtered through a Whatman 4A filter paper. The filtrate was submitted for GC analysis. Observations are given in Table C.

0.400 g $Fe_2(CO)_9$, 0 376 g $Co_2(CO)_8$, and 0.429 g $Mn_2(CO)_{10}$ were used. $Fe(CO)_5$ was measured volumetrically into 50 mL of synthetic test blend. 0.26 mL $Fe(CO)_5$ were used. $NaMn(CO)_5$ was generated in situ by dissolving 0.09 g NaOH into 50 mL ethanol and adding 0.429 g $Mn_2(CO)_{10}$. 50 mL synthetic test blend was added and the solution was acidified with 0.05 mL H_2SO_4 to form $HMn(CO)_5$. $HCo(CO)_4$ was formed and reacted as described for $MnH(CO)_5$. 0.376 g $Co_2(CO)_8$ were used.

Several labile species exist in solution in equilibrium after acidification of sodium carbonylates These species are very reactive hydridocarbonyls.

8. Hydrogenation In Presence of Metal Cabonyls
1000 psig H_2, 100°C

A 1-litre magnedrive autoclave, available from Autoclave Engineers was used for the hydrogenations. This autoclave was fitted with two 300 mL sample bombs. One was used to introduce the sample to the autoclave, which was attached to the gas inlet, the other was used to collect the liquid after hydrogenation and was attached to the dipleg.

Before any hydrogenations were carried out, the autoclave was cleaned with hydrocarbon solvent, methanol and methylene chloride. After each reassembly, the system was pressure tested with 2000 psig N_2. The autoclave was purged to remove air by pressurizing with 200 psig N_2, followed by evacuation with 30 psig vacuum.

The first hydrogenation was a blank run. 200 mL of synthetic test blend were added to the sample introduction bomb and the bomb was fitted between the hydrogen inlet line and the autoclave. The sample collection bomb was attached to the dipleg. 1000 psig H_2 was introduced to the autoclave through the sample collection bomb thereby also introducing the test blend.

The mixture was stirred at medium speed and the temperature was raised to 100°C. The 1000 psig hydrogen and 100°C were maintained for the reaction time. The pressure was dropped to 200 psig and the vented gases were passed through a caustic scrubber and released to the atmosphere. A liquid sample was taken and the remaining pressure was released.

The sample collection bomb was removed and the contents transferred to a 250 mL bottle. The sample was allowed to sit overnight before being filtered through Watman 4A filter paper. The filtrate was submitted for GC analysis. Results are given in Table 18.

The autoclave was purged with 50 psi N_2 for 15 minutes, and rinsed with hydrocarbon solvent, methanol and methylene chloride. The sample bombs were also washed with terpolene, methanol and methylene chloride. The sample collection bomb was reattached to the autoclave dipleg.

1.50 g $Co_2(CO)_8$ were dissolved in 200 mL of synthetic test blend, in a 250 mL Erlenmeyer flask. This mixture was poured into the sample introduction bomb and the bomb was fitted between the autoclave and the hydrogen inlet line. The hydrogenation was carried out as described for the blank.

For hydrogenations in the presence of $Mn_2(CO)_{10}$ or $Fe(CO)_5$ the procedures were identical to the one described for $Co_2(CO)_8$. 1.71 g $Mn_2(CO)_{10}$ and 1.05 mL of $Fe(CO)_5$ were used.

Due to low solubility in the synthetic test blend, 1.60 g $Fe_2(CO)_9$ and 200 mL synthetic test blend were added through the open top of the autoclave. The lid was bolted shut and the system was pressure-tested with nitrogen at 2000 psig. The autoclave was purged with nitrogen to remove all traces of oxygen and the mixture was hydrogenated as outlined for the blank.

1.50 g $Co_2(CO)_8$ were dissolved in 200 mL ethanol. 0.50 g KOH were added and the solution was mixed until all components were dissolved. The ethanol solution and 200 mL synthetic test blend were added through the open top of the autoclave. The lid was bolted shut, the autoclave was pressure-tested and purged with nitrogen. The mixture was hydrogenated as described for the blank.

$HMn(CO)_5$ was generated in the same manner as $HCo(CO)_4$. 1.71 g $Mn_2(CO)_{10}$ were utilized with 0.50 g KOH in 200 mL ethanol.

TABLE A

Observations During Contacting of Metal Chlorides with Synthetic Test Blend

COMPOSITION	OBSERVATIONS	
Grams Metal Chloride mL Synthetic Test Blend (STB)	Reaction at room temperature, 1 hour	Reaction at 200°C, 2 hours
0.375 g $CuCl_2.2H_2O$ 50 mL Standard Test Blend	$CuCl_2.2H_2O$ became black S.T.B. became grey	$CuCl_2.2H_2O$ became black S.T.B. became dark brown
0.565 g $FeCl_3.6H_2O$ 50 mL Standard Test Blend	$FeCl_3.6H_2O$ became yellow S.T.B. became cloudy and yellow	$FeCl_3.6H_2O$ became black S.T.B. became dark brown
0.417 g $SnCl_2$ 50 mL Standard Test Blend	$SnCl_2$ became yellow S.T.B. became cloudy and yellow	$SnCl_2$ became black S.T.B. became dark brown
0.300 g $ZnCl_2$ 50 mL Standard Test Blend	$ZnCl_2$ became yellow S.T.B. became cloudy and yellow	$ZnCl_2$ became black S.T.B. became dark brown
0.689 g C_6H_5HgCl 50 mL Standard Test Blend	Solution produced white emulsion filtrate was clear and colourless	Solution became black
0.583 g C_2H_5HgCl 50 mL Standard Test Blend	Solution became purple	Solution became purple

TABLE B

Observations After 1:1 Extraction with Polor Organic Solvents
Containing 10% Excess Metal Chloride

Solvent / Metal Chloride	DMSO	DMF	FURFURAL	ACETONITRILE
Blank	Upper phase clear Lower phase yellow No emulsion	Upper phase clear Lower phase Yellow No emulsion	Upper phase clear Lower phase black No emulsion	Upper phase yellow Lower phase clear No emulsion
$FeCl_2.2H_2O$	Upper phase clear Lower phase tan No emulsion	Upper phase clear Lower phase brown No emulsion	Upper phase clear Lower phase black No emulsion	Upper phase brown Lower phase clear No emulsion
$FeCl_3.6H_2O$	Upper phase clear Lower phase yellow No emulsion	Upper phase clear Lower phase brown No emulsion	Upper phase clear Lower phase black No emulsion	Upper phase brown Lower phase clear No emulsion
$SnCl_2$	Upper phase clear Lower phase yellow No emulsion	Upper phase clear Lower phase tan No emulsion	Upper phase clear Lower phase black No emulsion	Upper phase brown Lower phase clear No emulsion
$ZnCl_2$	Upper phase clear Lower phase yellow No emulsion	Upper phase clear Lower phase yellow No emulsion	Upper phase clear Lower phase brown No emulsion	Lower phase tan Lower phase clear No emulsion
C_2H_5HgCl	Upper phase clear	Upper phase clear	Upper phase clear	Upper phase clear
C_6H_5HgCl	Upper phase clear Lower phase red	Upper phase clear Lower phase red	Upper phase clear Lower phase red	Full amount of C_6H_5HgCl not soluble Upper phase red Lower phase clear

TABLE C

Appearance of Synthetic Test Blend After
Reaction with 10% Excess Metal Carbonyls

OBSERVATIONS

Metal Carbonyl	Room temperature, 30 mins.	100°C, 10 min.
$Fe(CO)_5$	Golden red solution	Yellow solution
$Fe_2(CO)_9$	Yellow solution	Bright green solution, black precipitate
$CO_2(CO)_8$	Dark red solution, black precipitate	Pale clear yellow solution, black precipitate
$Mn_2(CO)_{10}$	Yellow solution	Green solution, black precipitate
$HMn(CO)_5$	Yellow solution	Dark brown solution
$HCo(CO)_4$	Brownish red solution and precipitate	Dark yellow solution, brown precipitate

RESULTS AND DISCUSSION

In order to evaluate the removal of problematic components from a mixture of hydrocarbons, a blend of known composition was prepared and used in separation experiments. The blend consisted of a mixture of four aromatic nitrogen species, (carbazole, 2-methyl indole, 7,8-benzoquinoline and N-ethyl carbazole) two aromatic sulphur species (benzothiophene and dibenzothiophene) and two aliphatic sulphur species, (dodecylmercaptan and dinonyl sulfide). All problematic components were dissolved in Syncrude light distillate to form a synthetic test blend which contained between 50 and 250 ppm nitrogen or sulphur from each of the eight problematic species (Table 1).

The hydrocarbon matrix (Table 2) was a highly saturated Syncrude derived light distillate. Due to the extent of its hydrogenation, it contained only 11 ppm sulphur and 1.3 ppm nitrogen which, relative to the problematic components added, were negligible. Furthermore, the hydrocarbon composition of this material was largely cycloparaffinic (73.3 wt.%) and monoaromatic (19.3 wt.%). The large concentration of saturates proved to be troublesome in dissolving aromatic problematic components. As a results, compounds chosen for the synthetic test blend had to be soluble and concentrations of species were adjusted to insure precipitation due to solubility did not occur.

The other criteria for selecting problematic components were that they be difficult to remove and yet readily quantified. The four nitrogen species selected - carbazole, 2-methylindole, 7,8-benzoquinoline and N-ethylcarbazole - were readily resolved by gas chromatography (Table 3). Also, these materials were thought to be difficult to eliminate due to both nitrogen type and steric factors. Carbazole, 2-methylindole and N-ethylcarbazole all contain acidic or pyrrolic type nitrogen. Carbazole would be the most acidic compound by virtue of its three aromatic rings. 2-methylindole would be less acidic and even less reactive to metals due to steric hinderance of its methyl group, while N-ethylcarbazole should be completely inactive because it is completely substituted and any reaction with the nitrogen centre would be unfavoured since it would need to overcome some of the resonance energy of the molecule. 7,8-benzoquinoline, a basic nitrogen species, was also thought to be difficult to remove because the nitrogen position is also sterically hindered by the third aromatic ring. As a result, removal of these four species with metals was thought to pose a challenge. For a discussion on steric effects, see J.E. Huheey, Principles of Structure and Reactivity, Harper & Row; 1972, p.216.

Problematic sulphur components were much more soluble in the hydrocarbon matrix than the nitrogen species As a result aromatic sulphur species - benzothiophene and dibenzotriophene - were added at 100 ppm S concentration while aliphatic sulphur species - dodecylmercaptan and dinonylsulphide - were added at 250 ppm S levels These concentrations of materials were in large excess of the 11 ppm S found in the hydrocarbon matrix which was ignored in sulphur elimination calculations. Separation of the species by gas chromatography was adequate (Table 4); however, detector response was not linear which resulted in greater experimental error. The dodecylmercaptan concentration could not be adequately determined in this manner since it was readily oxidized and was calculated by difference from a total sulphur determination. Determination of dodecylmercaptan concentrations proved very problematic because of its reactivity.

A summary of the problematic components, their structure and properties is given in Table 5 for both nitrogen and sulphur species.

Low Severity Precipitation

Precipitation of problematic component at low severity conditions (1 h, 25°C) was attempted by complexation with metal chlorides. The cations evaluated included hard metals such as Fe_{+3}, Sn^{+2} and Zn^{+2}, borderline metals such as Cu^{+2} and soft metal species such as $EtHg^{+}$ and $\emptyset Hg^{+}$. Hard metals complex with hard ligands (N species) while soft metals complex with soft ligands (S species). In terms of hydrolysis constants or metal cation acidity, these metals could be ranked as follows (Table 6):

$$Fe^{+3} > EtHg^{+} \cong \emptyset Hg^{+} > Sn^{+2} > Cu^{+2} > Zn^{+2}$$

Results of the removal of problematic components by low severity precipitation with metals ions are listed in Table 8 and displayed graphically in Figure 1. The data show that nitrogen species are approximately one third removed while sulphur species are not affected except for dodecylmercaptan, which is 16-36% removed.

The base metals (Cu, Fe, Sn, Zn) eliminate between 12 and 44% of carbazole, 7,8-benzoquinoline and N-ethylcarbazole in the synthetic test blend. With 2-methylindole, removal is affected only with Fe^{+3} and Zn^{+2}. In general the order of removal of nitrogen species was:

$$Fe^{+3} > Zn^{+2} \cong Sn^{+2} \cong Cu^{+2}$$

This generally follows the order of cation hydrolysis except for Zn^{+2}. EtHgCl has no effect on component removal and ØHgCl is only marginally effective at removing 2-methylindole.

For the problematic sulphur components, only dodecylmercaptan, the most labile and reactive of the sulphur species, was eliminated. The order of elimination for metal ions was:

$$Fe^{+3} > Sn^{+2} > Cu^{+2} > Zn^{+2}$$

which is the exact order of metal hydrolysis and therefore a reaction such as:

$$RSH + M(H_2O)_6^{x+} \rightarrow (H_2O)_5\ M\text{-}SR^{(x-1)+} + H_3O^+$$

could be postulated for mercaptan elimination. Removal of other sulphur species failed because no metal complexes formed under these conditions.

<u>High Severity Precipation</u>

The severity of precipitation conditions was increased by increasing the reaction temperature to 200°C and the residence time to 2 h. This resulted in greater removal of all nitrogen species, except N-ethylcarbazole, and a greater elimination of dinonylsulfide. However, even at these more forcing conditions no one metal eliminated all problematic components uniformly.

The nitrogen species capable of complexation - carbazole, 2-methylindole and 7,8-benzoquinoline are all better eliminated than in low severity tests, particularly for $CuCl_2$. Increased temperature and residence time increased these three species elimination from 36, 65, 44% to 52, 100, 92% for $FeCl_3$ and from 26, 0, 32% to 58, 95, 98% for $CuCl_2$. Overall, the order of metal elimination was found to be:

$$Fe^{+3} \cong Cu^{+2} > Zn^{+2} > Sn^{+2} > \text{Ø}Hg^{+} > EtHg^{+}$$

which was distinctly different for the low severity precipitation, particularly for copper.

The reversal of N-ethylcarbazole elimination with more severe conditions is surprising. At low severity, base metals removed from 30-35% of the N-ethylcarbazole. At high severity, virtually none was removed. N-ethycarbazole is not likely to complex with a metal ion since it has no lone pair available for complexation and cannot readily lose a proton. Therefore, one can speculate that the superior low temperature removal of N-ethylcarbazole is due to the formation of a charge transfer complex or agglomerate. At higher temperatures the solubility of both species in the hydrocarbon matrix increases and no removal is noted. This could be substantiated by using a more polar or aromatic hydrocarbon matrix in both low and high temperature precipitations.

Precipitation of dinonylsulphide with these metals increased dramatically with increased severity. EtHgCl removed it quantitatively while $ZnCl_2$, ØHgCl and $SnCl_2$ eliminated 65, 44 and 40% of this species. The order of metal elimination was

$$EtHgCl > ZnCl_2 > \text{Ø}HgCl \cong SnCl_2 > FeCl_3 \cong CuCl_2$$

and can be attributed to the soft or polarizable nature of mercury, zinc and tin and their affinity for aprotic sulphur ligands. Removal of dodecylmercaptan tended to follow the order precipitation established at low severity:

$$Fe^{+3} > Cu^{+2} > Sn^{+2} > Zn^{+2}$$

It should be noted that the relative activity of copper and tin have reversed presumably due to temperature. None the less, removal roughly follows the order of metal cation hydrolysis, again suggesting mercaptan elimination is due to proton exchange complexation and precipitation occurring.

EtHgCl also shows some ability to eliminate dibenzothiophene; however, no reduction of benzothiophene occurs.

Solvent Extraction of Problematic Components

Selective removal of problematic components from the hydrocarbon matrix was also attempted by solvent extraction. As well as contacting the synthetic test blend with solvent, solvents in which metal chlorides were dissolved were also tested. The metal chloride was used so that metal chloride/problematic component complexes if formed would enhance the degree of problematic component extraction.

i) Dimethylsulfide (DMSO)

Extraction data for DMSO and DMSO/metal chloride solutions are listed in Table 10 and displayed graphically in Figure 3. DMSO alone removes carbazole and 2-methylindole quantitatively from the synthetic test blend at a 1/1 solvent/oil ratio. 7,8-benzoquinoline and N-ethylcarbazole are also largely removed (92 and 90%, respectively). All metal ion containing solutions extracted carbazole and 2-methylindole equally well; however, the extraction of 7,8-benzoquinoline and N-ethylcarbazole were slightly depressed. The increase in temperature may enhance extractions for the DMSO/metal chloride solutions as it did for precipitation but this effect was not evaluated.

Extractions of benzo- and dibenzothiophene were 100 and 16% respectively. Benzothiophene extractions were similar for all DMSO/metal chloride solutions except that of $FeCl_3$ where it was depressed to only 63% removal. This depression was parallelled for dibenzothiophene which was only 11% for DMSO/$FeCl_3$ versus 16% for DMSO alone. Other metal ions in DMSO enhanced the removal of dibenzothiophene, especially EtHgCl which quantitatively removed it and $ZnCl_2$ which removed 71%. Overall the effect

of metal chlorides on dibenzothiophene removal was

$$EtHgCl > ZnCl_2 > CuCl_2 \cong \emptyset HgCl \cong SnCl_2 > blank > Fe^{+3}$$

The superior affinity of $EtHg^+$ for sulphur even when compared to $\emptyset Hg^+$ can be attributed to the electron donating ability of the ethyl group relative to the electron withdrawing function of the phenyl group. Superior sulphur removal may be possible with t-butyl or perfluoromethyl-mercuric ions.

Overall DMSO alone is a very selective and effective solvent particularly for nitrogen heterocycles.

ii) Acetonitrile

Extraction of problematic components with acetonitrile followed a pattern similar for that established with DMSO and its solutions, especially for nitrogen species (Table 11, Figure 4). For acetonitrile itself, carbazole and 2-methylindole were quantitatively removed while 7,8-benzoquinoline and N-ethylcarbazole were largely removed (68 and 69%, respectively) but not to the same extent as with DMSO. All metal chloride acetonitrile solutions also remove carbazole and 2-methylindole as well as acetonitrile alone and as well $CuCl_2$, $FeCl_3$ and $SnCl_2$ acetonitrile solutions removed 7,8-benzoquinoline quantitatively have enhanced removal of N-ethylcarbazole. The combination of acetonitrile and $SnCl_2$ was particularly effective in nitrogen elimination.

Acetonitrile was also more effective at removing aromatic sulphur than aliphatic sulphur species. Removal of benzothiophene and dibenzothiophene was 54 and 44% for acetonitrile, respectively, while dodecylmercaptan and dinonylsulfide elimination were only 21 and 12%. Addition of Cu^{+2}, Fe^{+3}, Sn^{+2} and Zn^{+2} to acetonitrile enhanced the removal of benzothiophene slightly (3-6%), dibenzothiophene even more (4-9%) and dodecylmercaptan most of all (11-30%). The removal of dinonylsulphide was actually depressed by the presence of these metal atoms. This set of experiments also showed the efficacy of problematic sulpur compound removal with alkyl and aryl mercuric chlorides. EtHgCl in acetonitrile enhance benzothiophene, dibenzothiophene and dinonylsulphide removal by 10, 28 and 17% respectively while ØHgCl increased these removals by only 4, 15 and 1%. Clearly EtHgCl is the superior metal for removing sulphur compounds.

Acetonitrile is a very promising solvent for removal of problematic components by virtue of its low boiling point (81.6°C) it can be readily separated from higher boiling materials. However, it does pose some drawbacks, namely, it contains a large amount of nitrogen which can contaminate product and it can be hazardous particularly if contacted with acid since it will generate HCN.

iii) Dimethylformamide (DMF)

Problematic component extraction with DMF was superior to that of any solvent tested for both nitrogen and sulphur species evaluated (Table 12, Figure 5). DMF alone, quantitatively removed carbazole, 2-methylindole, benzothiophene, dibenzothiophene and dodecylmercaptan. Furthermore, 7,8-benzoquinoline and N-ethylcarbazole are also largely removed (90 and 86% removal, respectively). Only dinonylsulphide removal is poor (7%) but this was enhanced by the presence of metal ions, particularly stannous chloride. Nitrogen species removal remained constant for all DMF, DMF/metal chloride solutions studied. Similarily, the removal of benzothiophene and dibenzothiophene was also quantitative for all solutions studied. Dodecycl mercaptan removal was depressed for Cu^{+2}, Fe^{+3} and Zn^{+2} containing DMF solutions but was unaffected and quantitative for the Sn^{+2}/DMF solution. For dinonylsulphide, the only aliphatic apolar component, removal increased from 7% for DMF to 19% for the Zn^{+2}/DMF solution. The order of extraction for metal containing solutions and this species was:

$$Sn^{+2} \cong Fe^{+3} > Zn^{+2} \cong \text{ØHg}^{+} > \text{EtHg}^{+} > Cu^{+2} > \text{blank}$$

The poor extracting ability of the Zn^{+2}, $EtHg^{+}$ and Cu^{+2} solution are not typical of previous work.

iv) Furfural

Removal of problematic components with furfural above is quite effective (Table 13, Figure 6) but not as effective as with DMF. Extraction of carbazole, 2-methylindole, benzothiophene and dibenzothiophene are complete. The removal of 7,8-benzoquinoline and N-ethylcarbazole are large, 86 and 83% respectively which are slightly less than those obtained for DMF and DMSO. Furfural extraction of aliphatic sulphur species, dodecylmercaptan and dinonylsulphide is also quite good 32 and 48%.

Addition of metals chlorides to furfural enhances the extraction of some problematic species while decreasing the removal of others. All metals containing furfural solutions quantitatively removed 7,8-benzoquinoline while depressing the removal of N-ethylcarbazole. Similarly, the removal of all sulphur species was generally depressed. Extraction of dodecylmercaptan was observed to be:

$$Fe^{+3} >> Zn^{+2} > Sn^{+2} > Cu^{+2} > \text{Blank}$$

This generally parallels the extraction order observed for DMSO but is different than that observed for removal by precipitation in that Zn^{+2} is much more active in removing the species.

v) Solvent Evaluation

Extraction data for neat solvents: DMSO, acetonitrile, DMF and furfural are shown in Figure 7 for removal of the eight problematic components studied from the synthetic test blend. Results indicate, based on % removal as the sole criteria, that DMF is the superior solvent. This is due to the quantitative removal of carbazole, 2-methylindole, benzothiophene, dibenzothiophene and dodecylmercaptan. As well both 7,8-benzoquinoline and N-ethylcarbazole were also largely removed (90 and 86%, respectively). DMSO and to a slightly lesser extent furfural, were nearly as effective at removing nitrogen, but none approached DMF in the ability to remove sulphur species.

Low Severity Precipitation with Metal Carbonyls

Transition metal carbonyls were also evaluated for both nitrogen and sulphur component elimination. These carbonyls included iron ($Fe(Co)_5$ and $Fe_2(Co)_9$) cobalt ($Co_2(CO)_8$) and manganese ($Mn_2(CO)_{10}$), as well as attempted generation of the hydrocarbonyls of cobalt ($HCo(CO)_4$) and manganese ($HMn(CO)_5$). Some properties of these materials are listed in Table 8.

Removal of nitrogen species did not occur with $Fe(CO)_5$ $Fe_2(CO)_9$ and $Mn_2(CO)_{10}$ (Table 14, Figure 8). $Co_2(CO)_8$ did remove some carbazole and 2-methylindole but was ineffective in removing 7,8-benzoquinoline and N-ethylcarbazole. Only the hydridocarbonyl compounds, $HCo(CO)_4$ and $HMn(CO)_5$ effectively removed carbazole, 2-methylindole and 7,8-benzoquinoline but could remove no N-ethylcarbazole.

Carbonyl compounds particularly those of cobalt and manganese, were much more effective at removing sulphur species. Dimanganese decacarbonyl removed all the dinonylsulphide and dibenzothiophene from the test blend as well as 44% of the benzothiophene. Similar results obtained with dicobalt octacarbonyl showed 100, 66 and 41% removal of these species, respectively.

Iron carbonyls and the "hydridocarbonyls" were not nearly as effective at removing these sulphur species.

In general none of the carbonyl species tested are selective for both nitrogen and sulphur compound removal. The combination of $Mn_2(CO)_{10}/HMn(CO)_5$ may be and further work with managanese species may be in order.

High Severity Precipitation with Metal Carbonyls

Increasing the severity of precipitation with metal carbonyls and the synthetic test blend did not enhance markedly the removal of problematic species (Table 15, Figure 9) and results track those obtained at low severity. Dicobaltoctacarbonyl and dimanganese decacarbonyl quantitatively removed dibenzothiophene and dinonylsulphide while removing 44% of the benzothiophene. These results are very similar to those obtained at low severity. Hydridocarbonyls were somewhat less effective at removing nitrogen compounds and this may be due to their decreased stability with temperature or the reduced reaction time.

Of particular interest at high severity is the increased activity of $Fe(CO)_5$. Removal of carbazole, benzothiophene and dinonyl sulphide increased with the increased reaction temperature. It is surprising that $Fe_2(CO)_9$ in spite of its reactivity did not react. This may be due to the rate of solid-liquid reactions versus those of liquid-liquid reactions. This limitation may be overcome by using even higher reaction temperatures up to approximately 300°C which again may be worthwhile scoping.

Overall, metal carbonyls and hydridocarbonyls do not appear to be selective at both nitrogen and sulphur compound removal.

Problematic Component Elimination with Metal Carbonyl Hydrogenation

The synthetic test blend was hydrogenated in the presence of metal carbonyls at 100°C, P_{H_2} = 1000 psig for 2 hours. These rather mild conditions were used to determine whether or not metal carbonyls or carbonyl hydrides (generated in situ) had any catalytic activity. As well, a blank hydrogenation run was performed in order to evaluate the removal due to hydrogenation alone.

The blank run with the synthetic test blend showed that sulphur species were readily eliminated with no catalyst while nitrogen species were virtually unaffected.

In the blank run 73% of dodecylmercaptan and 36% of dinonyl-sulphide were removed as were approximately 10% of each of the aromatic sulphur species. Nitrogen species were not removed at all in the blank run. Dodecylmercaptan was removed to a large extent in all tests. These results are indicative of the ease of desulphurization of mercaptans and benzothiophenes relative to aromatic sulphur as well as the ease of desulphurization relative to dentrogenation.

Catalytic activity was not enhanced markedly for any of the carbonyl species evaluated except $HCo(CO)_4$. In this case carbazole, 7,8-benzoquinoline and N-ethylcarbazole elimination were increased to 20, 37 and 29%, respectively. Dodecylmercaptan removal was also increased to 92%.

Of the hydrogenation catalysts tested at these mild conditions $HCo(CO)_4$ had the most activity and while it was not great, future work at more severe conditions may be worth evaluating.

CONCLUSIONS

1. Removal of aromatic nitrogen and sulphur species from a hydrocarbon matrix, was best achieved by solvent extraction.

2. Dimethylformamide (DMF) was the most active solvent effectively removing most problematic components except dinonylsulphide.

3. Dissolution of metals into solvents enhanced the extraction of some sulphur species, but only marginally.

4. Dimanganese decacarbonyl and dicobalt octacarbonyl were effective at removing dibenzothiophene and dinonylsulphide.

5. Hydridocarbonyls may be effective at removing basic nitrogen compounds such as 7,8-benzoquinoline due to their acidity.

6. Precipitation of problematic components with metal chlorides increased with temperature for all species, except N-ethylcarbazole, which decreased.

7. The order of reactivity of metals varies with temperature, particulary for copper.

8. Hydrogenation of problematic components at 100°C and 1000 psig H_2 in the presence of metal carbonyls was ineffective.

RECOMMENDATIONS

1. The combination of solvent extraction and mild conventional hydrogenation should be further studied since it may be a viable means of sequentially eliminating aromatic and aliphatic problematic components.

2. Work with hydridocarbonyls generated from their sodium salts should be undertaken to further evaluate their ability to eliminate nitrogen species.

3. A systematic study of solvent additives, with strong organic acids such as alkyl sulphonic acids, should be undertaken to determine if problematic component separations can be enhanced.

4. Hydrogenations and precipitation conditions should be evaluated under more severe conditions of temperature and pressure.

5. Other metallic precipitants such as lead, cadmium, thallium, bismuth and boranes should be tested.

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TABLE 1

Composition of 1000 ppm N/S Synthetic Test Blend

500 g Syncrude Light Distillate*

0.2985 g (50 ppm N) Carbazole
0.4685 g (100 ppm N) 2 Methyl Indole
0.3200 g (50 ppm N) 7,8 Benzoquinoline
0.6975 g (100 ppm N) N Ethyl Carbazole

0.2093 g (100 ppm) Benzothiophene
0.2873 g (100 ppm) Dibenzotriophene
0.7893 g (250 ppm) Dodecylmercaptan
1.1155 g (250 ppm) Dinonyl Sulfide

*Physical properties in Table 2

TABLE 2

Physical and Chemical Characteristics of Syncrude Light Distillate

Characteristic	Method Reference	Result
API Gravity	ASTM D1298	32.4
Density at 15°C, kg/L	ASTM D1298	0.8629
Flash Point, °C	ASTM D93	69
Cloud Point, °C	ASTM D2500	-39
Aniline Point, °C	ASTM D611	64.5
Viscosity, cSt @ 40°C	ASTM D445	3.15
Distillation, °C	ASTM D86	
IBP		191
10%		223
50%		274
90%		316
FBP		328
% Recovered		99.0
% Residue		0.6
% Loss		0.4
Sulfur, ppm	ASTM D3120	11
Nitrogen, ppm	ASTM D3431	1.3
Nickel, ppm	X-ray	<1
Vanadium, ppm	X-ray	<1
Composition (mass %)		
Paraffins		6.64
Cycloparaffins		72.31
Monoaromatics		19.30
Diaromatics		0.29
Triaromatics		1.32
Tetraaromatics		0.07
Aromatic Sulfur		0.07
		100.00

TABLE 3

Instrument Conditions for Determination of Nitrogen Compounds in Synthetic Test Blend

GC:	Varian 3700
Column:	50 m x 0.2 mm I.D. crosslinked methyl silicone
Temperature:	Initial: 70°C/0 min Rate: 4°C/min Final: 260°C/30 min
Detector:	Varian Thermoionic Specific Detector
Carrier:	Nitrogen at 1.0 mL/min
T.S.D. Hydrogen Flow:	4.5 mL/min
T.S.D. Air Flow:	175 mL/min
T.S.D. Bias Voltage:	-4.0
T.S.D. Temperature	230°C
Injection Port Temperature:	180°C

Compound Name	Retension Time (min.)	Response Factor (R_x)
Quinoline*	26.0	1.000
2 methylindole	31.0	2.1954
7,8 benzoquinoline	45.0	0.9650
Carbazole	45.8	1.1627
N-ethylcarbazole	46.7	0.8987

*Internal Standard

TABLE 4

Instrument Conditions for Determination of Sulfur Compounds in Synthetic Test Blend

GC:	Perkin Elmer 3920
Column:	S.S. 6' x 1/8" I.D. packed with 10% O.V. -101 on Chromosorb W, 60/180 mesh
Temperature:	Initial: 70°C/0 min Rate: 4°C/min Final: 250°C/16 min
Detector:	Perkin Elmer Flame Photometric Detector
Carrier:	Helium at 30 mL/min
F.P.D. Hydrogen Flow:	70 mL/min (30 psi)
F.P.D. Air Flow:	110 mL/min (72 psi)
Detector Temeprature:	250°C
Injection Port Temperature:	260°C

Response Functions For Sulfur Determination

Benzothiophene:

$$\log(\text{pk.ht.}) = 2.625\,[\log(\text{conc})] - 4.577$$

Dibenzothiophene:

$$\log(\text{pk.ht.}) = 1.924\,[\log(\text{conc})] - 3.445$$

Dinonyl Sulfide:

$$\log(\text{pk.ht.}) = 2.169\,[\log(\text{conc})] - 4.348$$

TABLE 5

Problematic Components

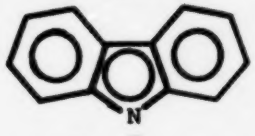
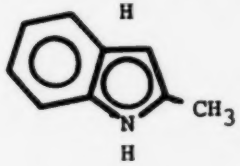
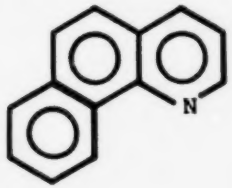
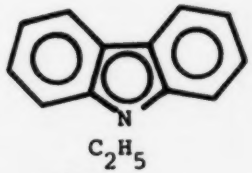
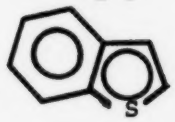
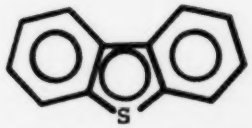
Compound	Formula	MW	Structure	mp(°C)	bp(°C)	$pK_a(H_2O)$	$pK_b(H_2O)$
1. Carbazole	$C_{12}H_9N$	167.21		245	355	19.9(DMSO)	13.8
2. 2-Methylindole	C_9H_9N	131.18		60	268	(-0.1?)	
3. 7,8-Benzoquinoline	$C_{13}H_9N$	179.22		52	349(721 mm)	4.25	
4. N-ethylcarbazole	$C_{14}H_{13}N$	195.27		68	190		
5. Benzothiophene	C_8H_6S	134.20		32	221	37.1	
6. Dodecylmercaptan	$C_{12}H_{26}S$		$CH_3(CH_2)_{11}SH$			12	
7. Dibenzothiophene	$C_{12}H_8S$	184.26		97	332	35.7	
8. Dinonylsulphide			$CH_2(CH_2)_8$-S-$(CH_2)_8CH_3$				

TABLE 6

Physical Properties of Metal Cations

Cation	z^2/r	pK_h	Acceptor Type (Arhland & Chatt)
Cu^{+2}	5.48	7.53	borderline
Fe^{+3}	13.85	2.19	A
Sn^{+2}	3.28	4.30	A
Zn^{+2}	5.33	9.60	A
$EtHg^{+}$	)	)	B
Hg^{2+}	) 3.92	Hg^{2+}) 3.70	
ϕHg^{+}	)	)	B

Ref: J.E. Huheey, Inorganic Chemistry: Principles of Structure and Reactivity, Harper & Row, p.214, 1972

TABLE 7

Properties of Metal Carbonyls

Compound	mp (°C)	Colour
$Fe(CO)_5$	-20.5	yellow
$Fe_2(CO)_9$	100(d)	orange
$CO_2(CO)_8$	51.52(d)	orange
$Mn_2(CO)_{10}$	154-155	yellow
$HCo(CO)_4$	-26	yellow
$HMn(CO)_5$	-24.6	colourless

Ref: I. Wender, P. Pino, Organic Synthesis vis Metal Carbonyls, Vol. 1, 1968, John Wiley

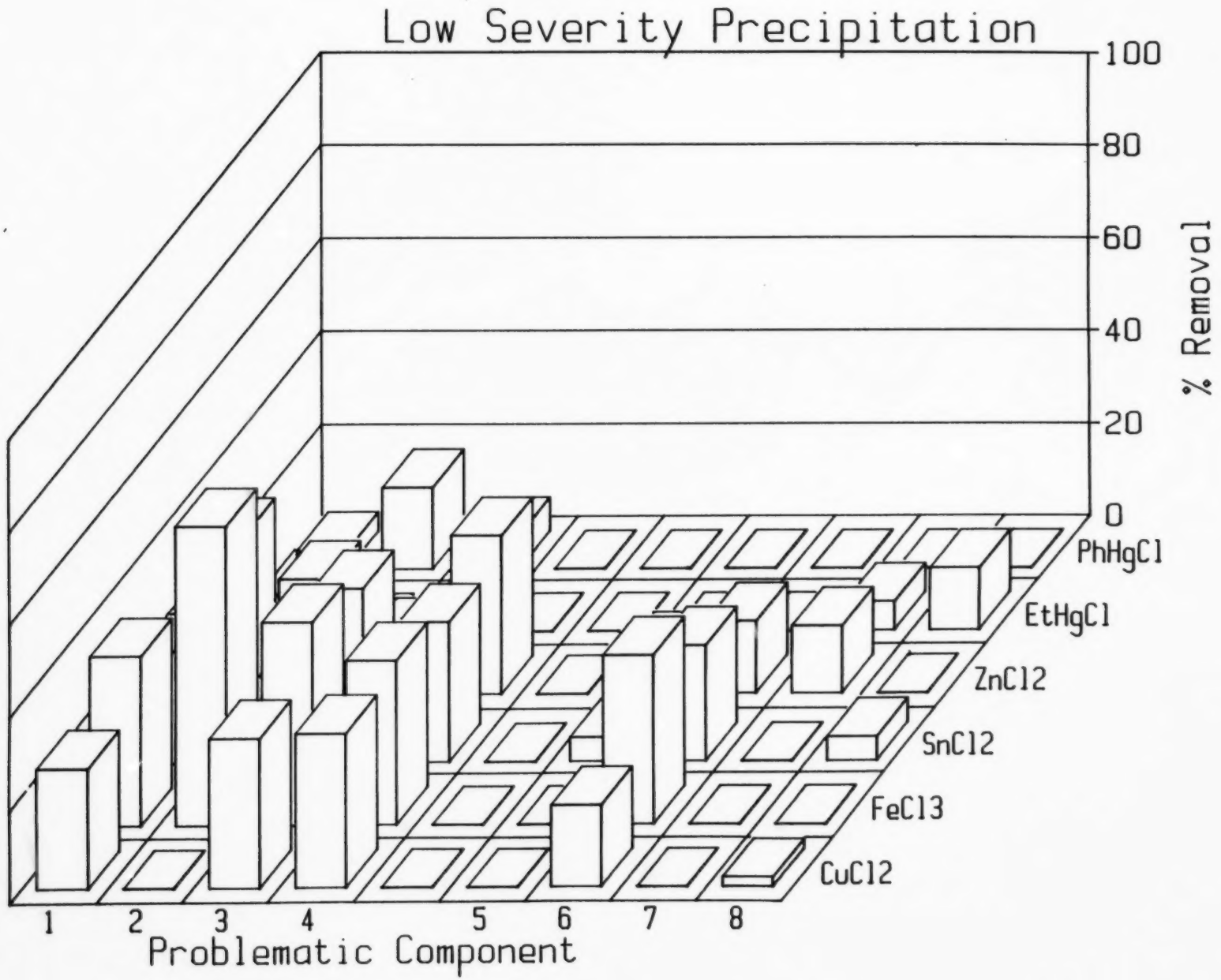
TABLE 8

Low Severity Precipitation
(1 h, 25°C)

Metal Chloride*	% Removal								
	Carbazole	2-Methyl Indole	7,8-Benzo Quinoline	N-Ethyl Carbazole	Benzo-Thiophene	Dodecyl Mercaptan	Dibenzo-Thiophene	Dinonyl-Sulfide	Total Sulfide
$CuCl_2.2H_2O$	26	0	32	33	0	18	0	2	7
$FeCl_3.6H_2O$	36	65	44	35	0	36	0	0	13
$SnCl_2$	24	0	38	30	5	25	0	5	11
$ZnCl_2$	34	25	12	34	9	16	15	0	17
C_2H_5HgCl	0	0	0	0	0	-	6	14	-
C_6H_5HgCl	4	18	7	0	0	-	0	0	-

* a 10% stiochiometric excess of metal chloride was used assuming 1:1 adducts formed.

FIGURE 1



1. Carbazole
2. 2-Methylindole
3. 7,8-Benzoquinoline
4. N-Ethylcarbazole
5. Benzothiophene
6. Dodecylmercaptan
7. Dibenzothiophene
8. Dinonylsulphide

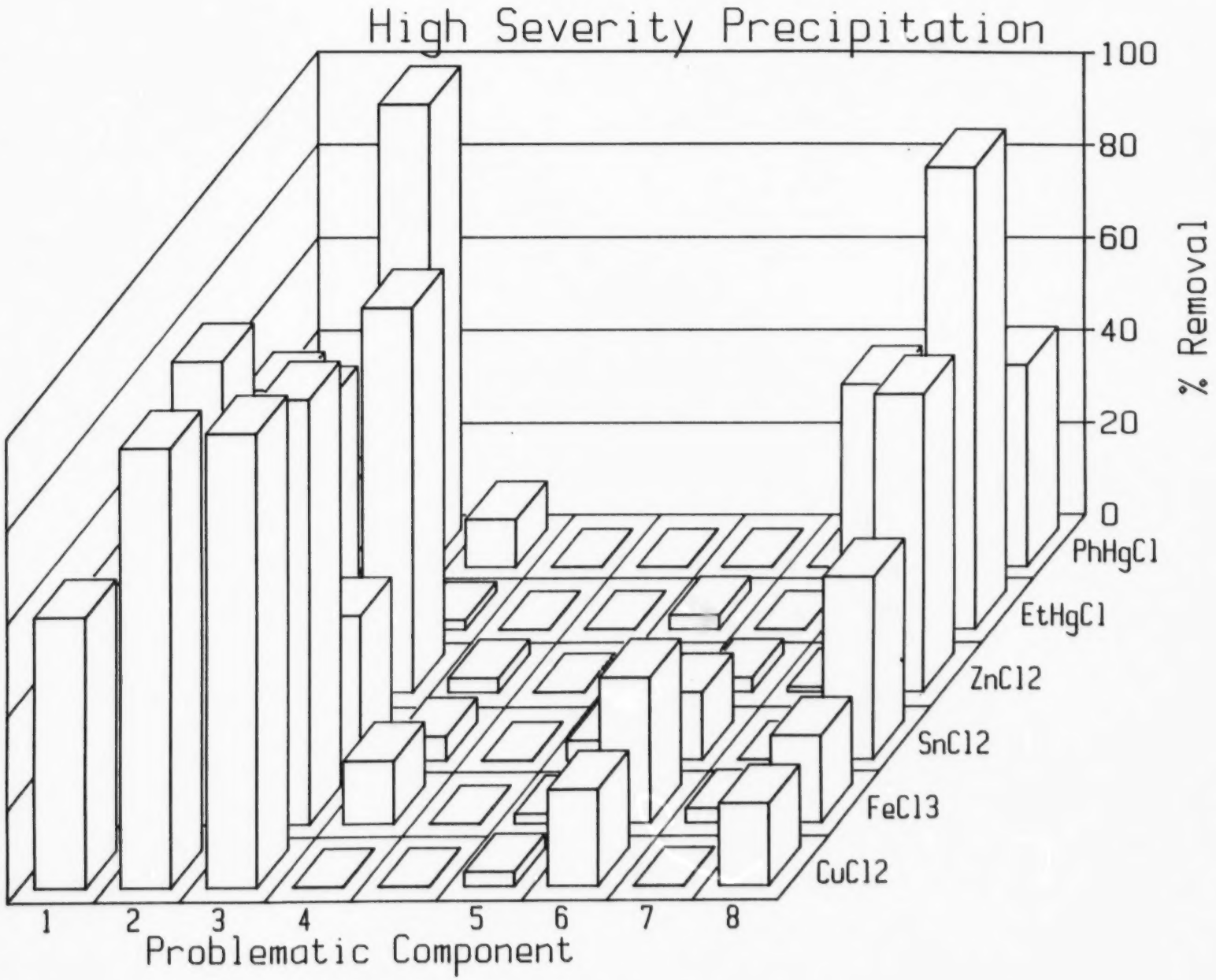
TABLE 9

High Severity Precipitation
(2 h, 200°C)

Metal Chloride*	% Removal								
	Carbazole	2-Methyl Indole	7,8-Benzo-Quinoline	N Ethyl Carbazole	Benzo-Thiophene	Dodecyl Mercaptan	Dibenzo-Thiophene	Dinonyl-Sulfide	Total Sulfide
$CuCl_2.2H_2O$	58	95	98	0	3	21	0	18	14
$FeCl_3.6H_2O$	52	100	92	14	2	31	3	19	18
$SnCl_2$	0	44	31	5	4	15	0	40	20
$ZnCl_2$	0	62	83	3	0	3	1	65	24
C_2H_5HgCl	52	4	2	0	3	-	53	100	-
C_6H_5HgCl	16	100	10	0	0	-	0	44	-

* a 10% stiochiometric excess of metal chloride was used assuming 1:1 adducts formed.

FIGURE 2



1. Carbazole
2. 2-Methylindole
3. 7,8-Benzoquinoline
4. N-Ethylcarbazole
5. Benzothiophene
6. Dodecylmercaptan
7. Dibenzothiophene
8. Dinonylsulphide

TABLE 10

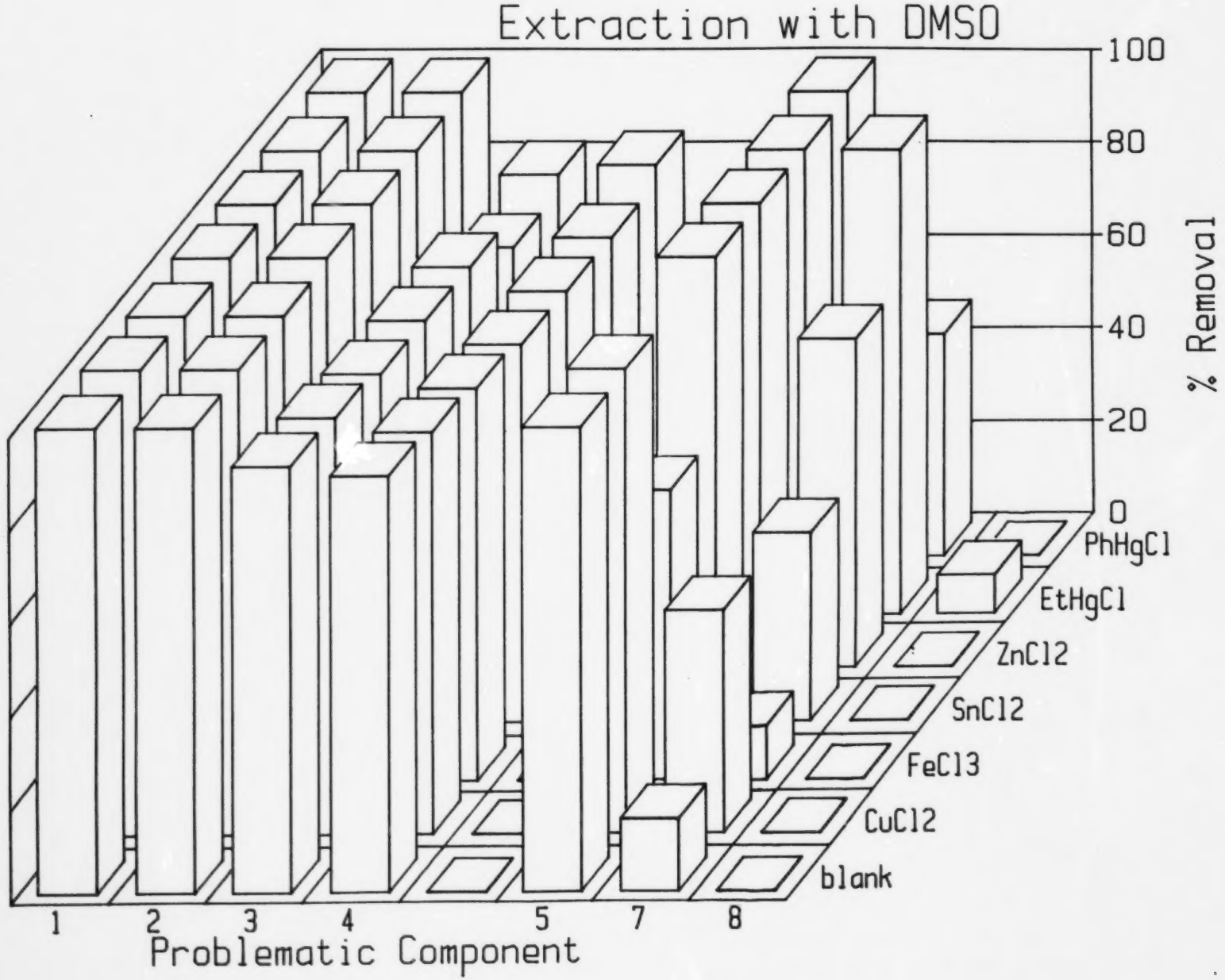
Extraction of Problematic Components with DMSO
(1 h, 25°C, solvent/oil = 1/1)

Metal Chloride+	% Removal**						
	Carbazole	2-Methyl Indole	7,8-Benzo-Quinoline	N Ethyl Carbazole	Benzo-Thiophene	Dibenzo-* Thiophene	Dinonyl Sulfide
Blank	100	100	92	90	100	16	0
$CuCl_2 \cdot 2H_2O$	100	100	90	86	100	48	0
$FeCl_3 \cdot 6H_2O$	100	100	88	84	63	11	0
$SnCl_2$	100	100	86	81	100	41	0
$ZnCl_2$	100	100	86	81	100	71	0
C_2H_5HgCl	100	100	79	81	100	100	8
C_6H_5HgCl	100	100	82	84	100	48	0

* % Removal may appear low due to background DMSO.

\+ Solvent contained 10% stiochiometric excess of metal chloride assuming 1/1 adducts form.

** Dodecylmercaptan could not be back calculated due to interference with DMSO.



1. Carbazole
2. 2-Methylindole
3. 7,8-Benzoquinoline
4. N-Ethylcarbazole
5. Benzothiophene
6. Dodecylmercaptan
7. Dibenzothiophene
8. Dinonylsulphide

TABLE 11

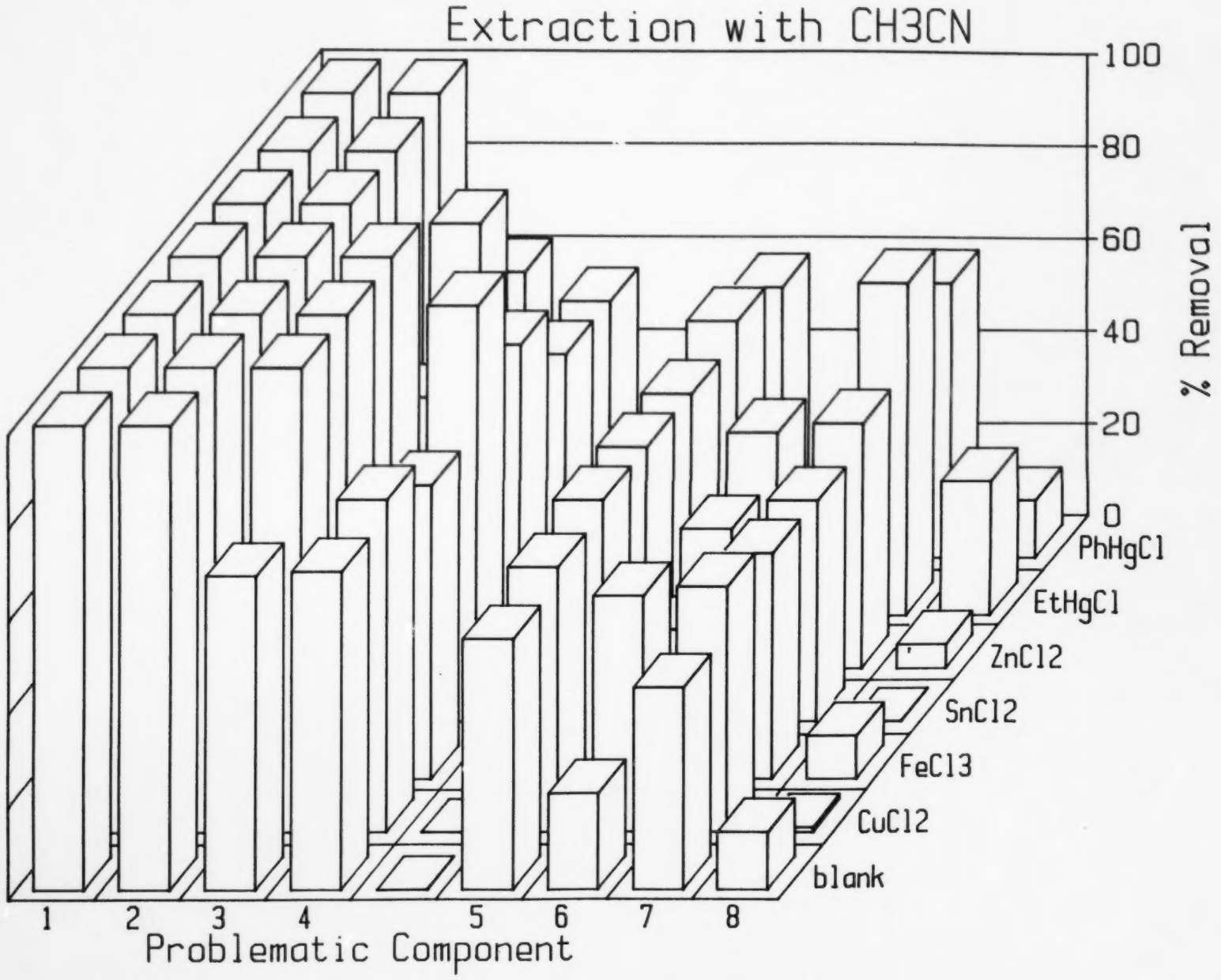
Extraction of Problematic Components with Acetonitrile
(1 h, 25°C, solvent/oil = 1/1)

Metal Chloride+	% Removal								
	Carbazole	2-Methyl Indole	7,8-Benzo-Quinoline	N Ethyl Carbazole	Benzo-Thiophene	Dodecyl Mercaptan	Dibenzo-Thiophene	Dinonyl-Sulfide	Total Sulfide
Blank	100	100	68	69	54	21	44	12	25
$CuCl_2.2H_2O$	100	100	100	72	57	51	53	1	34
$FeCl_3.6H_2O$	100	100	100	64	60	32	49	9	30
$SnCl_2$	100	100	100	90	59	42	48	0	30
$ZnCl_2$	100	100	58	70	59	51	53	5	35
C_2H_5HgCl	100	100	84	56	64	-*	72	29	-*
C_6H_5HgCl	100	100	61	55	58	-*	59	13	-*

* Sample size too small for X-ray Analysis

\+ Solvent contained 10% stiochiometric excess of metal chloride assuming 1/1 adducts form.

FIGURE 4



1. Carbazole
2. 2-Methylindole
3. 7,8-Benzoquinoline
4. N-Ethylcarbazole
5. Benzothiophene
6. Dodecylmercaptan
7. Dibenzothiophene
8. Dinonylsulphide

TABLE 12

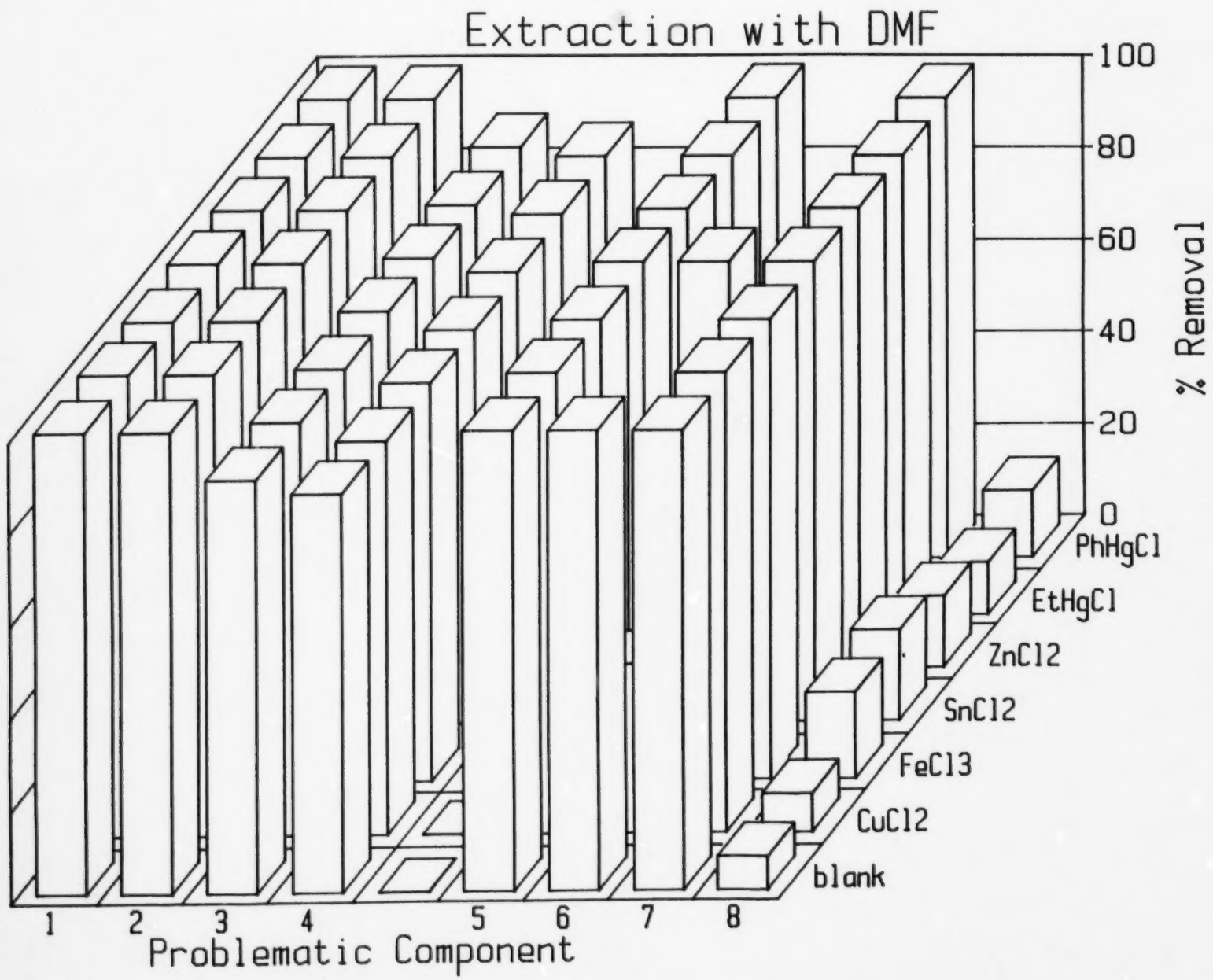
Extraction of Problematic Components with DMF
(1 h, 25°C, solvent/oil = 1/1)

Metal Chloride+	% Removal								
	Carbazole	2-Methyl Indole	7,8-Benzo-Quinoline	N Ethyl Carbazole	Benzo-Thiophene	Dodecyl Mercaptan	Dibenzo-Thiophene	Dinonyl-Sulfide	Total Sulfide
Blank	100	100	90	86	100	100	100	7	66
$CuCl_2 \cdot 2H_2O$	100	100	90	85	100	36	100	8	44
$FeCl_3 \cdot 6H_2O$	100	100	90	86	100	69	100	19	59
$SnCl_2$	100	100	90	85	100	100	100	20	73
$ZnCl_2$	100	100	90	86	100	32	100	16	45
C_2H_5HgCl	100	100	90	87	100	-*	100	11	-*
C_6H_5HgCl	100	100	90	87	100	-*	100	15	-*

* Sample size too small for X-ray Analysis

+ Solvent contained a 10% stiochiometric excess of metal chloride assuming 1/1 adducts formed.

FIGURE 5



1. Carbazole
2. 2-Methylindole
3. 7,8-Benzoquinoline
4. N-Ethylcarbazole
5. Benzothiophene
6. Dodecylmercaptan
7. Dibenzothiophene
8. Dinonylsulphide

TABLE 13

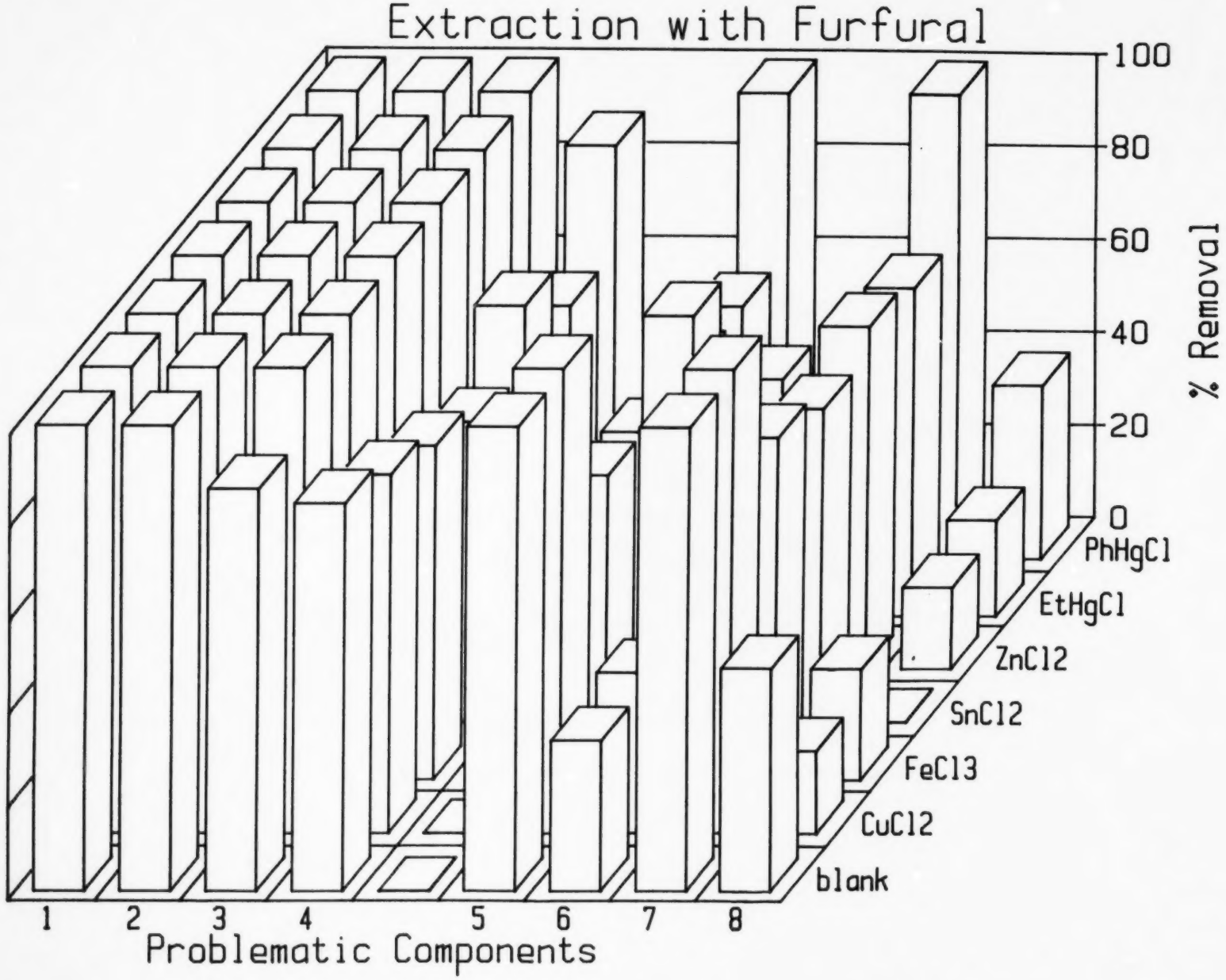
Extraction of Problematic Components with Furfural
(1 h, 25°C, solvent/oil = 1/1)

Metal Chloride+	% Removal								
	Carbazole	2-Methyl Indole	7,8-Benzo-Quinoline	N Ethyl Carbazole	Benzo-Thiophene	Dodecyl Mercaptan	Dibenzo-Thiophene	Dinonyl-Sulfide	Total Sulfide
Blank	100	100	86	83	100	32	100	48	56
$CuCl_2 \cdot 2H_2O$	100	100	100	77	100	34	100	18	47
$FeCl_3 \cdot 6H_2O$	100	100	100	72	66	100	74	24	27
$SnCl_2$	100	100	100	65	62	40	68	0	32
$ZnCl_2$	100	100	100	78	66	62	74	18	48
C_2H_5HgCl	100	100	100	67	67	-*	71	21	-*
C_6H_5HgCl	100	100	100	89	100	-*	100	38	-*

* Sample size too small for X-ray Analysis

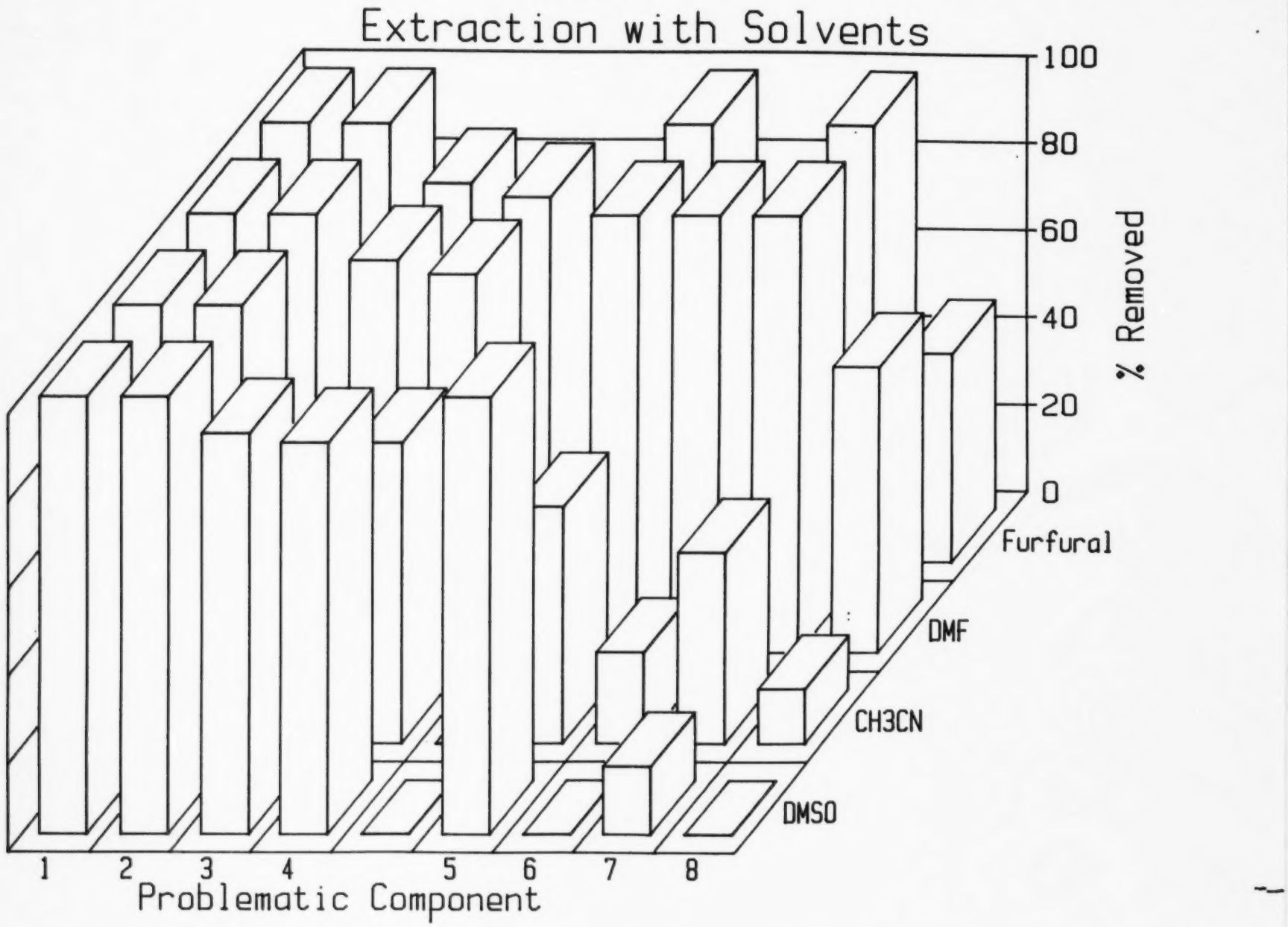
\+ Solvent contained a 10% stiochiometric excess of metal chloride assuming 1/1 adducts formed.

FIGURE 6



1. Carbazole
2. 2-Methylindole
3. 7,8-Benzoquinoline
4. N-Ethylcarbazole
5. Benzothiophene
6. Dodecylmercaptan
7. Dibenzothiophene
8. Dinonylsulphide

FIGURE 7



1. Carbazole
2. 2-Methylindole
3. 7,8-Benzoquinoline
4. N-Ethylcarbazole
5. Benzothiophene
6. Dodecylmercaptan
7. Dibenzothiophene
8. Dinonylsulphide

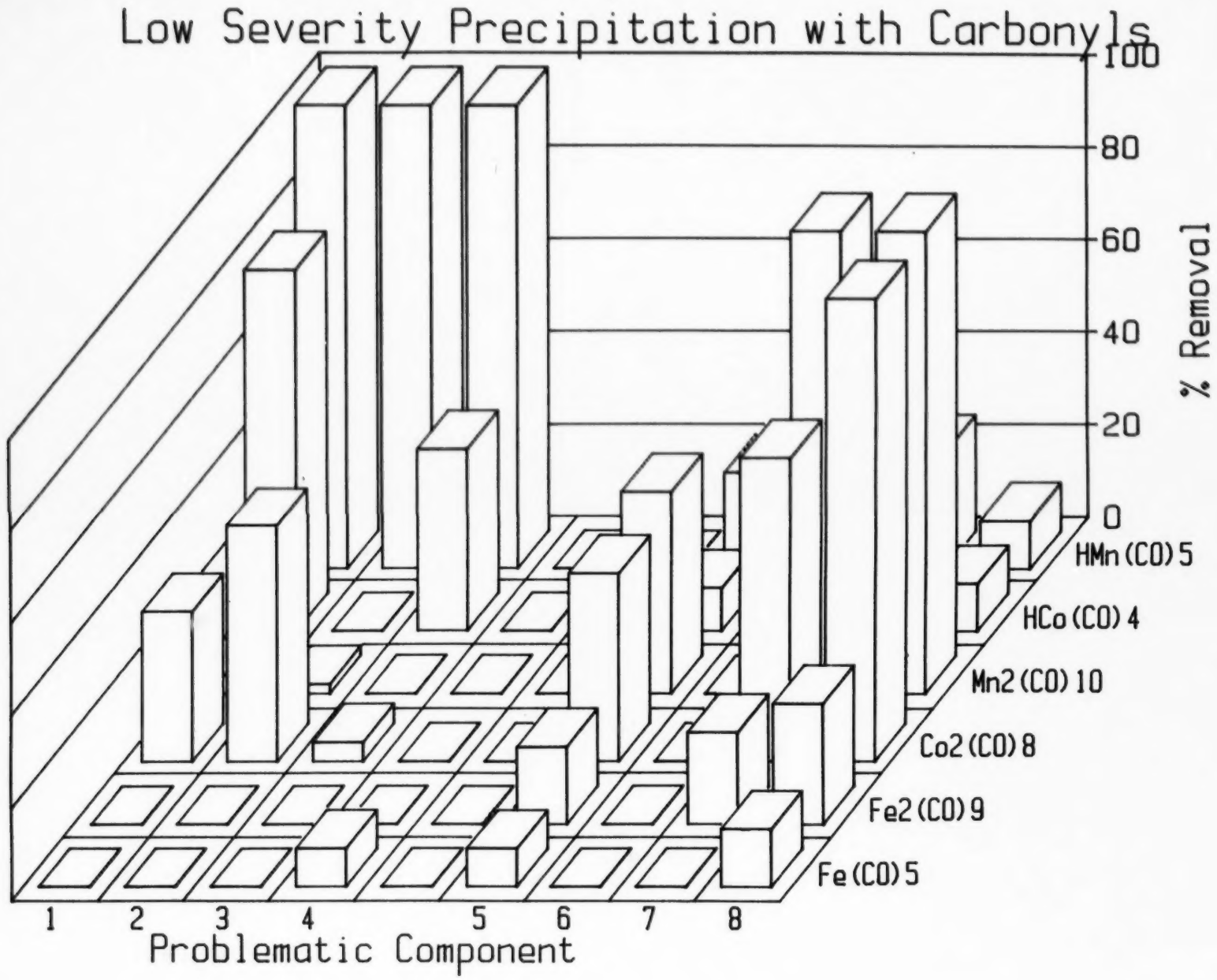
TABLE 14

Low Severity Precipitation with Metal Carbonyls
(25°C, 30 min.)

Metal Carbonyl+	% Removal						
	Carbazole	2-Methyl Indole	7,8-Benzo-Quinoline	N-Ethyl Carbazole	Benzo-Thiophene	Dibenzo-Thiophene	Dinonyl-Sulfide
$Fe(CO)_5$	0	0	0	8	8	0	12
$Fe_2(CO)_9$	0	0	0	0	17	20	26
$Co_2(CO)_8$	32	51	4	0	41	66	100
$Mn_2(CO)_{10}$	4	2	0	0	44	100	100
$HCo(CO)_4$	78	0	40	0	9	8	10
$HMn(CO)_5$	100	100	100	0	21	25	10

+ 10% stiochiometric excess of metal carbonyl was used assuming a 1/1 adduct formed with each metal atom.

FIGURE 8



1. Carbazole
2. 2-Methylindole
3. 7,8-Benzoquinoline
4. N-Ethylcarbazole
5. Benzothiophene
6. Dodecylmercaptan
7. Dibenzothiophene
8. Dinonylsulphide

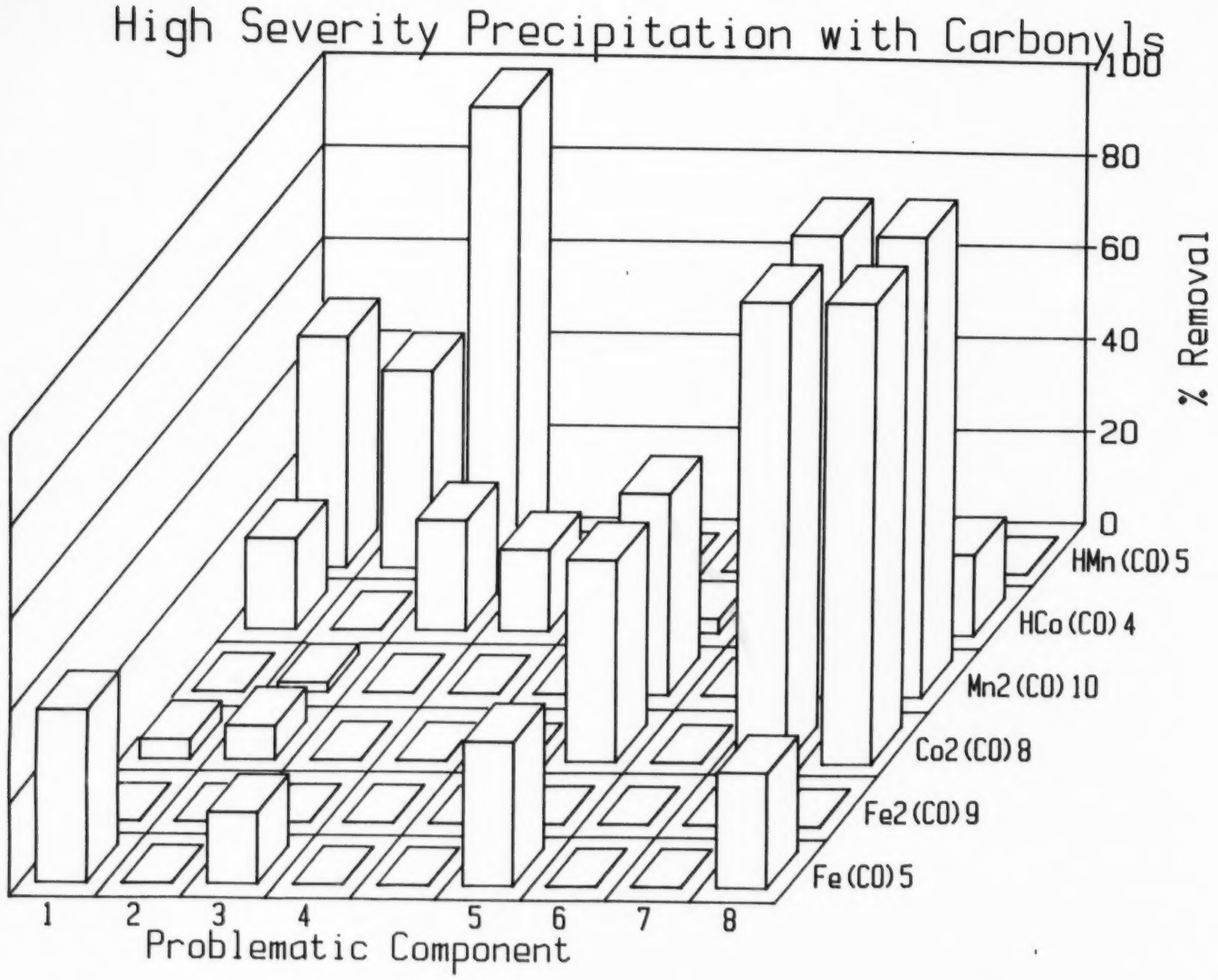
TABLE 15

High Severity Precipitation with Metal Carbonyls
(100°C, 10 min.)

Metal Carbonyl+	% Removal						
	Carbazole	2-Methyl Indole	7,8-Benzo-Quinoline	N Ethyl Carbazole	Benzo-Thiophene	Dibenzo-Thiophene	Dinonyl-Sulfide
$Fe(CO)_5$	38	0	16	0	31	0	25
$Fe_2(CO)_9$	0	0	0	0	0	0	0
$Co_2(CO)_8$	4	7	0	0	44	100	100
$Mn_2(CO)_{10}$	0	2	0	0	44	100	100
$HCo(CO)_4$	20	0	24	18	3	0	18
$HMn(CO)_5$	50	43	100	0	0	0	0

+ 10% stiochiometric excess of metal carbonyl was used assuming a 1/1 adduct formed with each metal atom.

FIGURE 9



1. Carbazole
2. 2-Methylindole
3. 7,8-Benzoquinoline
4. N-Ethylcarbazole
5. Benzothiophene
6. Dodecylmercaptan
7. Dibenzothiophene
8. Dinonylsulphide

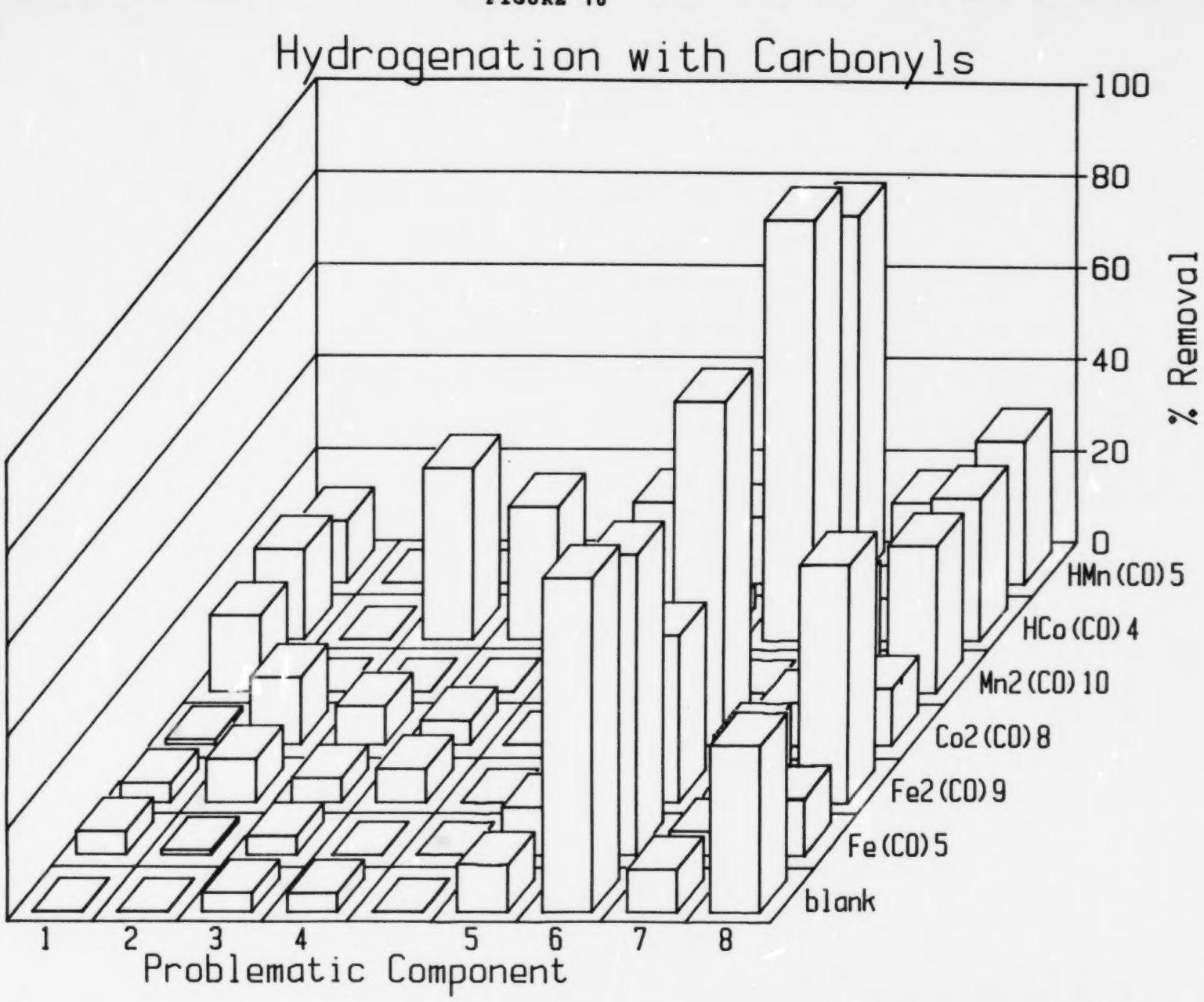
TABLE 16

Hydrogenation of Synthetic Test Blend with Metal Carbonyls
(100°C, 2 h, P_{H_2} = 1000 psig)

	% Removal								
Metal Carbonyl+	Carbazole	2-Methyl Indole	7,8-Benzo-Quinoline	N Ethyl Carbazole	Benzo-Thiophene	Dodecyl Mercaptan	Dibenzo-Thiophene	Dinonyl-Sulfide	Total Sulfide
Blank	0	0	4	4	10	73	9	36	41
$CO_2(CO)_8$	1	15	8	5	6	75	9	12	51
$Mn(CO)_{10}$	17	0	0	0	0	42	0	22	32
$Fe(CO)_5$	5	1	4	0	10	66	5	12	30
$Fe_2(CO)_9$	4	9	5	7	15	36	15	52	35
$HCo(CO)_4$	20	0	37	29	5	92	9	31	45
$HMn(CO)_5$	14	0	0	0	15	80	18	31	44

+ 10% stiochiometric excess of metal carbonyl was used assuming a 1/1 adduct formed with each metal atom.

FIGURE 10



1. Carbazole
2. 2-Methylindole
3. 7,8-Benzoquinoline
4. N-Ethylcarbazole
5. Benzothiophene
6. Dodecylmercaptan
7. Dibenzothiophene
8. Dinonylsulphide